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Tetraphenylene Ring Flip Revisited

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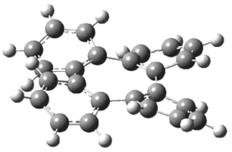


The ring flip barrier of a series of benzannulated cyclooctatetraenes is investigated at B3LYP and MP2. The ring flip of tetraphenylene proceeds through a nonplanar transition state, contrary to a previous study, with a large barrier of 78.6 kcal mol^{-1}.

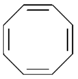
Cyclooctatetraene **1** is a tub-shaped polyene,[1] adopting this geometry to avoid antiaromaticity in the planar structure.[2] Interchange among the four equivalent D_{2d} tub structures occurs through two planar transition states: a D_{4h} structure that corresponds to ring flipping and a D_{8h} structure that corresponds to the π-bond shifting process.[3] These processes have been examined with a number of computational techniques.[3–6] The barrier for the ring flip process is estimated to be 17.1 kcal mol^{-1} at MP2-CASSCF(8,8)/6-31G*.[3] B3LYP/6-31G* predicts a somewhat smaller barrier of 10.5 kcal mol^{-1}.

Recently in this journal, Bau, Wong, and co-workers reported a detailed study of the ring flip of tetraphenylene **6**.[7] They prepared the dimethyl-substituted analogue **6a** and isolated the two enantiomers. Since each enantiomer has a notable optical activity ([α]$_D$ ±23), the ring flip process would racemize the compound and lead to a lowering of the optical rotation. Subjecting (***R***)-**6a** to 550 °C for 4 h led to no detectible change in the optical activity, indicative of a very large barrier to the ring flip process. Their B3LYP/6-31G(d,p) computations appear to corroborate this: the energy difference between the tub ground state of **6** and its planar structure (**6pl**) is 135 kcal mol^{-1}.

TABLE 1. Relative Energies, Point Group, and Number of Imaginary Frequencies of Ring Flip Critical Points[a]

	planar		nonplanar TS	
	E(B3LYP)	*E*(MP2)	*E*(B3LYP)	*E*(MP2)
1	10.55, D_{4h} (1)	15.62		
2	9.06, C_{2v} (1)	15.51		
3	9.22, D_{2h} (1)	16.91		
4	30.20, C_{2v} (2)	38.85	28.50, C_2 (1)	33.66
5	58.68, C_{2v} (4)	69.54	39.13, C_2 (1)	43.99
6	134.04, D_{4h} (5)	148.40	76.48, D_4 (1)	78.61

[a] Energies in kcal mol^{-1} relative to the tub-shaped ground state structure; number of imaginary frequencies in parentheses.



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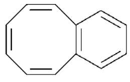

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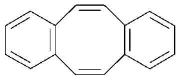

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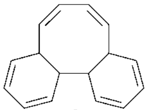

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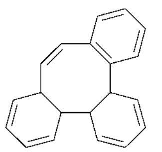

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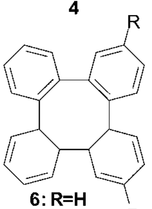

6: R=H
6a: R=Me

We were struck by the very large value of this barrier, a value significantly larger than a typical C−C bond strength, especially given that the process is formally just rotations about bonds. We report here DFT and MP2 computations of the ring flip process for the series of benzannulated cyclooctatetraenes **1**−**6**. All structures were fully optimized within the constraints of appropriate point groups at B3LYP/6-31G(d,p).[8] Analytical frequencies were performed on all structures to confirm their nature and obtain zero-point vibrational energies (ZPE, used without corrections). All of these structures were reoptimized at MP2/6-31G(d,p) and their energies were corrected for ZPE by using the B3LYP values.[9] The energies of the critical points along the ring flip process, relative to the tub-shaped ground state, are listed in Table 1. All computations were performed with the Gaussian-03 suite.[10]

The predicted ring flip barrier of **1** is similar to the previous work, with the MP2 barrier 1.5 kcal mol^{-1} lower than the MP2-CASSCF[3] estimate. A single benzannulation (**2**) or two benzannulations in the *a*,*e* positions (**3**) have little effect on the barrier. For the three compounds **1**−**3** the ring flip transition state is planar. (The structures of the ground state (tub) and planar transition state of **3**, representative of **1**−**3**, are shown in Figure 1). B3LYP consistently underestimates the barrier height by about 6 kcal mol^{-1} relative to the MP2 estimate of about 16 kcal mol^{-1}.

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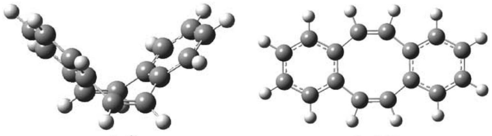
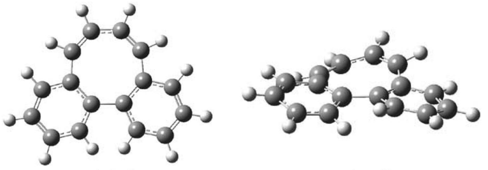
10.1021/jo900413d CCC: $40.75



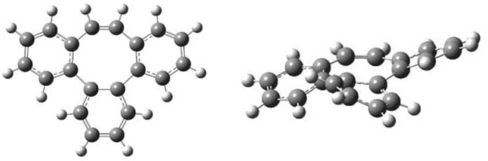
3 C_{2v} **3pl** D_{2h}

FIGURE 1. Optimized structures of **3**.



4pl C_{2v} **4ts** C_2

FIGURE 2. Optimized structures of **4**.



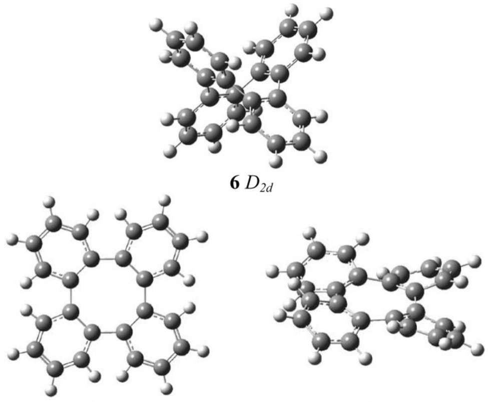
5pl C_{2v} **5ts** C_2

FIGURE 3. Optimized structures of **5**.

This situation is dramatically different for **4**, which has the two benzannulations in the *a*,*c* positions. Here the *ortho* and *ortho′* hydrogens can interact, analogous to the *ortho,ortho′* hydrogen interaction in biphenyl.[11] This unfavorable interaction leads to biphenyl being nonplanar, and one might be concerned about this unfavorable contact in the planar geometry of **4**. The planar C_{2v} geometry **4p** (Figure 2) places the two *ortho* hydrogens only 1.53 Å apart, a very close contact! This unfavorable interaction results in this C_{2v} structure possessing two imaginary frequencies. Optimization with the reduced symmetry of C_2 leads to the true ring flip transition state **4ts** (Figure 1), having a single imaginary frequency. By canting the two phenyl rings, the *ortho* hydrogens can be positioned farther apart (B3LYP: 1.70 Å; MP2: 1.82 Å). The planar structure lies 38.8 kcal mol^{-1} (30.2 kcal mol^{-1} at B3LYP) above the tub ground state, but the true barrier height through the C_s transition state is 33.7 kcal mol^{-1} (28.5 kcal mol^{-1} at B3LYP).

The tribenzannulated cyclooctatetraene **5** has two sets of adjacent *ortho* hydrogen atoms. Its planar C_{2v} structure **5pl** has four imaginary frequencies and is correspondingly very high in energy, 69.5 kcal mol^{-1} (58.7 kcal mol^{-1} at B3LYP) above the tub ground state (Figure 3). The *ortho*,*ortho′* H···H distance is 1.46 Å. Reducing the symmetry to C_2 allows the phenyl rings to cant, thereby increasing the offending H···H distance to 2.10 Å (2.06 Å at B3LYP). This twisting decreases the energy of the structure substantially; the barrier for the ring flip of **5** through the C_2 structure **5ts** is 44.0 kcal mol^{-1} (39.1 kcal mol^{-1} at B3LYP).

We now turn to tetraphenylene **6**, the object of study by Bau and Wong.[7] The tub-shaped D_{2d} structure, shown in Figure 4, is a true local energy minimum, having only real frequencies. Given the results for **4** and **5** it is not surprising that the planar D_{4d} structure **6pl** (Figure 4) is not a true transition state. Rather, it has five imaginary frequencies. This planar structure has four pairs of clashing *ortho* hydrogens, and their separation is only 1.35 Å. To gauge the effect of these close contacts, we computed the energy of two benzene molecules oriented with a hydrogen on each directed at each other. When this H···H distance is 1.35 Å, the closest contact distance in **6pl**, the benzene dimer is 6.4 kcal mol^{-1} destabilized relative to two isolated benzene molecules. The four close H···H contacts thus substantively contribute to the high energy of **6pl**. In addition, each phenyl ring is significantly distorted in **6pl**; for example, their C−C−C angles are 113.3°, 130.4°, and 116.3°. We estimate the strain energy in the four phenyl groups as 83.8 kcal mol^{-1} (see the discussion of Table 2 below). Therefore, **6pl** is quite energetic and lies 148.4 kcal mol^{-1} (134.0 kcal mol^{-1} at B3LYP) above the tub-shaped conformer, in agreement with Bau and Wang.[7]



6 D_{2d}

6pl D_{4h} **6ts** D_4

FIGURE 4. Optimized structures of **6**.

TABLE 2. Strain Energy (kcal mol^{-1}) of Benzene in the Transition States of 2−6 and Total Strain Energy Due the Phenyl Groups

compd	benzene strain energy[a]	total phenyl strain energy[b]
2pl	5.59	5.59
3pl	4.46	8.91
4ts	14.31	28.63
5ts	22.90 (central) 9.59 (terminal)	42.08
6ts	20.37	81.48
6pl	30.95	83.81

[a] Computed by taking the MP2 energy difference between benzene of the geometry in the specific molecule and fully optimized benzene. The hydrogens in the benzylic position are arbitrarily placed 1.08 Å from C at the same angle and torsional angles as the carbon they are replacing. [b] Computed as the sum of the benzene strain energies, so for **5** it is twice the value of the terminal benzene plus the value of the central benzene.

A nonplanar transition state for the ring flip of **4**−**6** was anticipated by Müllen, Klärner, Roth, and co-workers in 1990.[12] Their MM2 study identified nonplanar transition states for the ring flip of **4**−**6**, though of C_1 symmetry. To find the true ring flip transition state for **6** one must reduce the symmetry of the planar structure to D_4. The optimized structure within this point group (**6ts**), shown in Figure 2, has all four phenyl rings canted in the same orientation, like the fins on a propeller or windmill. This tilting allows for the *ortho* hydrogens to move apart; the *ortho,ortho* H···H separation is 2.06 Å (2.05 Å at B3LYP). This makes the D_4 propeller much more stable than **6pl**; it lies 70 kcal mol^{-1} below the planar structure. It remains, however, quite energetic relative to the ground state tub structure. The true barrier for the ring flip through **6ts** is 75.8 kcal mol^{-1} (76.5 kcal mol^{-1} at B3LYP); the previous MM2 estimate of this barrier (65.9 kcal mol^{-1}) is in reasonable agreement. (MM2 also

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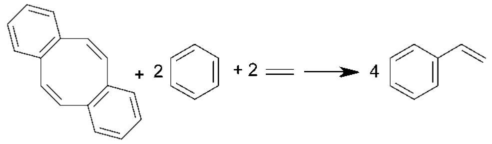
underestimated the ring flip barriers of **4** and **5** by about 5 kcal mol^{-1}, ref 12). So while Bau and Wong[7] drastically overestimated the ring flip barrier by making an erroneous assumption concerning the transition state, the very large *true* barrier (through **6ts**) is completely consistent with their main conclusion. This large barrier cannot be surmounted by heating and decomposition of tetraphenylene will occur instead.[7]

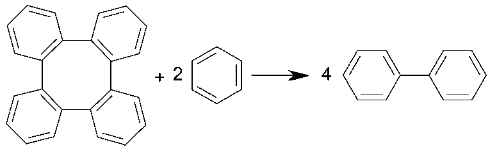
Despite the canting of the phenyl groups in **6ts**, which minimizes the *ortho,ortho′* hydrogen interactions, the barrier remains very high. Further, the ring flip barrier of cycloctatetraene increases with benzannulation (Table 1). What accounts for this trend?

First, we examine the effect of benzannulation on the ground state conformation. We assess this by examining the ring strain energies of **1**−**6** using the group equivalent[13] reactions 1−6 and the MP2 energies (all six reactions are shown in the Supporting Information; two examples are shown below). The ring strain energies of **1**−**6** are remarkably similar and small. Cyclooctatetraene **1** exhibits 2.43 kcal mol^{-1} of strain energy. The most strained is **3**, with a strain energy of 4.34 kcal mol^{-1}. The least strained is **6** and its strain energy is only 1.82 kcal mol^{-1}. Therefore, benzannulation has little effect on the strain energy in the ground state of these molecules.

Reaction 3



Reaction 6



The increase in ring flip barrier with increasing benzannulation must then originate in destabilization of the transition state. Examination of the geometries of the ring flip transition states of **2**−**6** reveals significant distortion of the phenyl rings, especially at the bridgehead positions. These formal sp^2 carbons must accommodate both angles greater than 130° for the 8-membered ring and angles often less than 115° within the 6-membered ring. These small angles in the 6-membered rings are to minimize the interaction of adjacent rings.

To assess the strain in the phenyl rings in the TSs of **2**−**6** we have computed the energy of benzene with the geometry of the phenyl group within the substituted cyclooctatetraene. The benzylic carbons are replaced by hydrogen atoms at a distance of 1.08 Å from the phenyl carbon, but retaining the angles and dihedral angles of the benzylic carbon. The strain energy is defined then as the difference in the MP2 energy of the distorted benzene and fully optimized benzene. These strain energies are listed in Table 2. The total strain energy of the transition states of **2**−**6** is computed as the sum of the component benzene strain energies.

The benzene strain energy in **2pl** and **3pl** is small, less than 6 kcal mol^{-1}, and results in little increase in the ring flip barrier. The benzene strain in **4ts** is substantial (14.3 kcal mol^{-1} per each ring) and the 20 kcal mol^{-1} of strain above that of **3pl** correlates to the increase in ring flip barrier in going from **3** to **4**.

The strain of the central benzene ring of **5ts** is almost 23 kcal mol^{-1} and with the modest strain of the two terminal benzene rings leads to a substantial strain in the ring flip transition state. Though the strain energy of the phenyl group of **6ts** is less than that of the central ring of **5ts**, since all four phenyl rings are equally strongly strained, the transition state of **6** contains an enormous degree of phenyl strain, approximately 81 kcal mol^{-1}. The ring flip of **6** has such a large barrier because there is simply no mechanism to avoid clashes between the adjacent phenyl rings. Canting the rings minimized the conflict between the *ortho* hydrogens, but the phenyl rings must distort to such a degree to maintain the 8-membered ring through the flipping process that the barrier is an insurmountable hill of nearly 80 kcal mol^{-1}.

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Supporting Information Available: Full citation for ref 10 and reactions 1−6, and coordinates of the B3LYP/6-31G(d,p) and MP2/6-31G(d,p) geometries of **1**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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